

Liquidus surface of FeO-Fe₂O₃-SiO₂-CaO slag containing Al₂O₃, MgO and Cu₂O at various oxygen partial pressures

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ABSTRACT

Liquidus surface of FeO-Fe₂O₃-SiO₂-CaO system is of special importance in general pyrometallurgy. It determines several industrial slags, such as “fayalite” slag, calcium ferrite slag, acidic and basic steel making slags as well as the newly proposed ‘ferrous calcium silicate slag’, which are all nominally based on this system. Nevertheless the liquidus surface of this system has been studied only in equilibrium with metallic iron or in air and the data at intermediate oxygen partial pressures are almost missing. In reductive smelting processes the above-mentioned slags were based on the liquidus surface of FeO-Fe₂O₃-SiO₂-CaO system in equilibrium with metallic iron. In oxidative matte smelting and in today’s modern trends of non-ferrous smelting such as continuous converting or white metal production, the characterization of the liquidus surface of this system at intermediate oxygen partial pressures becomes imperative. Furthermore the effect of minor oxides on the liquidus surface of this system has not been studied at higher oxygen potentials and confusing conclusions are found in literature even for low oxygen potentials. In this work a quantitative description of the liquidus surface of FeO-Fe₂O₃-SiO₂-CaO slag containing Al₂O₃, MgO and Cu₂O is carried out by means of a thermodynamic model at various oxygen partial pressures. Through a new type of easy-to-understand multicomponent phase diagrams it is shown that important differences exist between the liquidus surfaces of this system in reductive and oxidative conditions. It is also shown that minor components can have fundamentally different effects in reductive and oxidative conditions.

INTRODUCTION

The FeO-Fe₂O₃-SiO₂-CaO system is of special importance in general extractive metallurgy. Many existing industrial slags such as the “fayalite” slag, calcium ferrite slag, acidic and basic steel making slags as well as the newly proposed ‘ferrous calcium silicate slag’ are nominally based on this system. The liquidus surface of this system determines the operational windows of existing slags as well as the availability of new slags for more advanced technologies. Nevertheless the liquidus surface of this system has been studied only in equilibrium with metallic iron or in air and the data at intermediate oxygen partial pressures are almost missing. However, most of the industrial processes are carried out at intermediate oxygen potentials and not at limiting conditions of iron saturation or in air. For instance, most of the classical copper smelting and converting processes, especially the new modern ones such as continuous converting or white metal production, are carried out at oxygen partial pressures varying from 10⁻⁸ to 10⁻⁶ atm. The liquidus surface of these slags is however not known at these oxygen potentials. Metallurgists seem to have ignored the difference in the oxygen potential and its influence on the slag liquidus surface and continue to empirically use the liquidus surface of the above-mentioned system at iron saturation (oxygen partial pressures from 10⁻¹¹ to 10⁻¹² atm) in both reductive and oxidative processes. This is believed to be the reason for the confusion that exists today in the literature and industrial practice about the problem of “magnetite” precipitation which most of the time has been only empirically explained.

Most of the industrial slags also contain several amounts of minor oxides, which are introduced through the mineral concentrates, fluxes, dissolved refractories etc. These oxides significantly effect the liquidus surface of FeO-Fe₂O₃-SiO₂-CaO system and the operational windows of the slags. Nevertheless the effect of minor oxides on the liquidus surface of this system has not been studied at intermediate oxygen potentials and more confusing conclusions are found in literature even for low oxygen potentials since the difference between the reductive and oxidative conditions is not taken into account.

In previous work (1-3) the liquidus surface of the CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃-MgO system has been quantified along with the effect of CaO, Al₂O₃ and MgO as minor oxides at predominantly low oxygen potentials through a new type of multicomponent phase diagrams(1). The purpose of this work is to quantify for the first time the liquidus surface of CaO-FeO-Fe₂O₃-SiO₂ slag containing Al₂O₃, MgO and Cu₂O at various intermediate oxygen potentials. The quantification of the effect of oxygen potential and minor oxides on the slag liquidus surface as well as the clarification of the confusion that exists in today’s literature is also envisaged. This work will also serve the purpose of the quantification of the liquidus surface of the newly proposed ‘ferrous calcium silicate slag’ (4,5).

THERMODYNAMIC MODELING

A thermodynamic model consists of a set of model equations for the Gibbs energies of all phases in a multicomponent system as a function of temperature, composition and pressure. The parameters of the model equations are obtained by “optimization” in which all available thermodynamic and phase equilibria data in binary and ternary systems of a multicomponent system are evaluated simultaneously to provide a model where the data are self-consistent and obey thermodynamic principles. From these equations all the

thermodynamic properties and phase diagrams of simple systems can be reproduced and those of multi-component systems can be predicted. Technically this is realized by storing the model parameters in solution databases, which are then used along with pure component databases by a general Gibbs free energy minimization software that incorporates the model equations to calculate multi-component and multi-phase heterogeneous equilibria. This process is described in detail in previous publications (1-11).

Thermodynamic modeling is an interesting and useful tool for quantitative characterization of liquidus temperatures and other phase relations as well as thermodynamic properties. It offers three main advantages. Firstly, it considerably reduces the amount of the experimental work needed to characterize the above-mentioned properties over a wide range of compositions and temperatures. Based on the existing experimental data, the model employs thermodynamically and structurally correct interpolations and extrapolations to predict the liquidus temperature on several regions of composition and temperature where the data do not exist. Only a few new experimental data may be needed to verify and calibrate the model predictions in the multicomponent systems. As a consequence, the time and overall cost associated with a quantitative characterization of the liquidus surface in a wide range of compositions is decreased. Secondly, thermodynamic modeling can overcome some difficulties occurred during the measurements of the slag liquidus of the multicomponent slags. Usually these slags have steeply sloping surface whose placement depends on the stable primary phase. Not only is the appearance of the first solid phase difficult to detect, but in addition the liquidus temperature is so sensitive to compositional changes that normal errors in chemical analyses will result in data scatter. This explains the fact that the experimental liquidus data are usually quite scattered and difficult to correlate using simple empirical model.

In this work several new private models for the liquid and solid phases in the CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃-MgO system were developed by the authors. In addition, old private and FACT models were modified by the authors in the light of the new data (12) (to be published elsewhere). The modified quasichemical model (10) was used for the liquid slag. The compound energy formalism (14) as well as other polynomial models were used for modeling of solid phases. Private software(12) and FACT system (13) were used for the construction of the diagrams and the modeling process.

The predictions of the model were first verified against all available experimental data related specifically to the oxygen potential and minor oxides. This process was followed by the construction of simple polythermal projection and isothermal diagrams in order to quantify their effect on the liquidus temperature of the CaO-FeO-Fe₂O₃-SiO₂ slag and to quantitatively describe the important differences that exist between oxidative and reductive conditions.

EFFECT OF OXYGEN ON THE LIQUIDUS SURFACE OF FeO-Fe₂O₃-SiO₂-CaO SLAG

Experimental Verification of Model Predictions

Figures 1-3 show the liquidus isotherms in CaO-FeO-Fe₂O₃-SiO₂ system at 1300°C and at several oxygen partial pressures (10^{-8} , 10^{-7} and 10^{-6} atm) according to model

predictions and the recent experimental data of Tsukihashi (15). The data of Takeda et al.(16) and Takeda (17) in the limiting ternary systems are also shown. The agreement between the model and the experimental data is within experimental error limits. A disagreement though exist between the model and the data of Tsukihashi(15) at iron oxide-rich corner at oxygen partial pressure of 10^{-6} atm. However, taking into account the fact that the model agrees with the data of Takeda et al.(16) and Takeda(17) in the limiting ternary systems and the well-known fact that an increase in the oxygen partial pressure stabilizes magnetite, it can be said that, at this particular region, the experimental data may not be correct.

Some other experimental data on the liquid regions of this system at 1300°C and oxygen partial pressure of 10^{-7} atm has been reported by Shigaki et al.(18). These data do not agree with the data of Tsukihashi (15) in the quaternary system and those of Takeda et al. (16) and Takeda (17) on the limiting ternary systems, which, as shown above, satisfactorily agree with the model.

It should be noted that the above-mentioned model predictions are based exclusively on the binary and ternary sub-systems and the predicted diagrams at these oxygen partial pressures were constructed before the recent data of Tsukihashi(15) became available.

Polythermal Projection Diagrams

Figure 4 and 5 present two examples of the liquidus surface of CaO-FeO-Fe₂O₃-SiO₂ system at oxygen potentials of 10^{-8} and 10^{-5} atm by the means of a new type of multicomponent phase diagrams whose thermodynamic basis has been previously described (1). Each individual diagram directly gives the effect of CaO on the slag liquidus surface at constant oxygen potential and both give the effect of oxygen potential on this surface. It can be seen that six primary crystalline saturation areas are present, i.e. spinel, alpha-Ca₂SiO₄, wollastonite, Ca₃Si₂O₇, silica and wustite, and each of them has their own characteristics. Three important points can be easily made from these diagrams.

Firstly, contrary to the existing empirical belief, no fayalite or olivine surface exists at these oxygen potentials. This fact makes irrelevant the use of the term “fayalite” for iron-silica slags at these conditions. The name “fayalite” has always been used for the slags consisting of iron oxide and silica of composition near Fe₂SiO₄ regardless the exposed oxygen potential. In fact, this name is only meaningful at low oxygen potentials where the fayalite saturation surface exists. It can also be tolerated wherever the olivine area is present. In other situations, however, where only the spinel phase exists, its use should be employed with caution because it can lead to incorrect conclusions as the ones explained below. A meaningful name of the so-called “fayalite” slag at intermediate oxygen potentials might be spinel or magnetite slag. However taking into account the fact that the name “fayalite” has been repeatedly used in the past to “imagine” the composition of this slag, this name will continue to be used in this paper only in parenthesis (“F”) in order to expose its irrelevant meaning at intermediate oxygen potentials.

Secondly, contrary to the today’s general empirical belief, CaO does not decrease the liquidus temperature of smelting and converting slags in the spinel saturation area at intermediate oxygen potentials. As seen from the above diagrams, at constant Fe/SiO₂ ratios, CaO increases the slag liquidus temperature by about 4-5 degrees per each positive increment of 1%CaO. It decreases it only at high CaO contents near the Ca₂SiO₄ saturation surface,

which is the area of the newly proposed “ferrous calcium silicate slags (FCS)(4,5). In other words, additions of small amounts of CaO in the silica non-saturated slags at constant Fe/SiO₂ ratio do not decrease but instead increase the risk of spinel (magnetite) precipitation. This is in agreement with the experimental work of Maeda et al.(19) who conclude among others that the addition of CaO has no effect in suppressing the precipitation of Fe₃O₄. Only when the original slag composition lies on the silica saturation area, additions of CaO decrease the liquidus temperature as long as the composition holds on to this surface. As seen in the figures, in the silica saturation surface, at a constant Fe/SiO₂ ratio, an increase of CaO content by 1 wt% can cause a temperature decrease of about 40-50°C. Also, at a constant CaO content, an increase of Fe/SiO₂ ratio by 0.1 can cause a temperature drop of about 40-50°C. An increase of the oxygen partial pressure slightly suppresses this area. However, almost none of the slags in industrial processes have the original composition in the silica saturation area, since as explained below, the normal minor oxides that come from the raw materials suppress this area and place the original composition in the spinel surface. From this point on the additions of CaO would only increase the liquidus temperature of the slag at intermediate oxygen potentials.

Thirdly, the understanding of several factors that increase the risk of spinel (magnetite) precipitation in several processes is made easy from these diagrams. As it can be seen, in the spinel saturation area, at a constant CaO content, an increase of Fe/SiO₂ ratio increases the risk of spinel precipitation since it increases the liquidus temperature. This effect is non-uniform and is more pronounced at low Fe/SiO₂ ratios. A simple analysis of both diagrams shows that an increase of the oxygen potentials also increases the risk of spinel precipitation since it increases the slag liquidus temperature and enlarges the spinel saturation area. A drop in the operating temperature also increases the risk of spinel (magnetite) precipitation and this can be drastic at low oxygen potentials. As shown in Figure 5, only a slight decrease of the temperature from 1300 to 1275 or from 1275 to 1250°C decreases considerably the liquid regions and increases drastically the risk of magnetite precipitation.

From the above diagrams several other points are also worth noting since they can directly help several pyrometallurgical processes in order to select the most efficient operational window. In the wollastonite saturation area, at a constant Fe/SiO₂ ratio an increase of CaO content initially causes an increase of the liquidus temperature and after a certain content a decrease. This effect is not uniform and depends on the starting composition of the slag. At a constant CaO content an increase of Fe/SiO₂ ratio causes a non-uniform decrease of the liquidus temperature with a more pronounced effect at higher CaO contents. An increase of the oxygen potentials also suppresses this area. In the Ca₂SiO₄ saturation area, at a constant Fe/SiO₂ ratio, an increase of CaO content by 1% increases the liquidus temperatures by about 25 degrees. Again, this effect is not uniform and is less pronounced at high Fe/SiO₂ ratios and high oxygen partial pressures. At a constant CaO content an increase of Fe/SiO₂ ratio by 0.1 decreases the liquidus temperature by approximately 17 degrees in a non-uniform way. An increase of the oxygen potential slightly suppresses this area.

Isothermal diagrams

Figures 6 and 7 show the influence of oxygen partial pressure on the liquid regions at 1300°C. As can be seen, the liquid region decreases considerably with the increase of the oxygen partial pressure. This decrease is significant in the spinel saturation area even for slight increases of the oxygen potential and consequently the risk of magnetite precipitation

increases considerably. This explains several problems encountered in industrial practice with the spinel or magnetite (M) precipitation. However, another effect is visible nearby Ca_2SiO_4 surface, which corresponds to the newly proposed “ferrous calcium silicate slag”(4,5). The liquid region in this area increases slightly with the increase of the oxygen potential. In Figure 6 it is also noteworthy the transition from the wustite precipitation area to the spinel one along with the increase of oxygen potential.

Oxidative and reductive conditions

There is a fundamental difference between the effect of CaO in oxidative smelting and converting conditions, such as those in the present work where oxygen potentials vary between 10^{-8} - 10^{-6} atm, and reductive conditions where oxygen potentials are approximately below 10^{-9} atm. This is shown in Figure 8, which clearly demonstrates that, at a constant Fe/SiO₂ ratio, CaO decreases the liquidus temperature in reductive conditions (olivine precipitation surface) but it increases it in oxidative conditions (spinel saturation surface).

EFFECT OF Al_2O_3 ON THE LIQUIDUS SURFACE OF FeO-Fe₂O₃-SiO₂-CaO SLAG

Experimental Verification of Model Predictions

The model prediction of the liquid region in the FeO-Fe₂O₃-SiO₂-CaO-Al₂O₃ system containing 5% Al₂O₃, at 1300°C and oxygen partial pressure of 10^{-8} atm has been presented in Figure 9 along with the recent experimental data of Tsukihashi (15) that became available after the diagram was constructed. As can be seen the model predictions agree within experimental error limits with these experimental data except of two points in the iron oxide-rich corner, which is in fact outside the region of interest of this work. Further experimental measurements in this region and in the magnetite saturation area are suggested.

Shigaki et al.(18) measured the liquid region of CaO-SiO₂-Fe₃O₄ system containing 5% Al₂O₃ at oxygen partial pressure of 10^{-7} atm. The general form of the liquidus line of their diagram does not agree with the model predictions and the data of Tsukihashi (15). This was exactly the case with their data in the CaO-SiO₂-Fe₃O₄ system of the same work mentioned previously. Nevertheless the data of Shigaki et al.(18) qualitatively confirm the findings of the model that small alumina additions stabilize magnetite and reduce the liquidus region in the magnetite saturation area.

The model predictions also generally agree with some data in air atmosphere reported by Yang et al.(20) although they are outside the scope of the interest of this work.

Polythermal Projection Diagrams

Figure 10 and 11 present two examples of the liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃ system containing various constant amounts of Al₂O₃ at oxygen potential of 10^{-8} atm. It can be seen that five primary crystalline saturation areas are present i.e. spinel, alpha-Ca₂SiO₄, wollastonite, Ca₃Si₂O₇ and silica and each of them has their own characteristics. The following important points are worthy of note.

Contrary to some assertions in recent literature and contrary to its effect in reducing conditions(1-3), at a constant Fe/SiO₂ ratio, Al₂O₃ increases the slag liquidus temperature in the spinel saturation area at intermediate oxygen potentials. This increase is non-uniform and varies from 6 to 8 degrees per each positive increment of 1% Al₂O₃. It can also be seen that additions of Al₂O₃ enlarge the spinel saturation area and suppress the formation of solid silica by moving the silica boundary toward lower silica content. However this is associated with an increase of the liquidus temperature in the spinel surface and not with a decrease. Only, if the original composition of the slag lies in the silica surface, which, as mentioned above, is a rare case in industrial practice, additions of Al₂O₃ decrease the liquidus temperature and suppress the silica saturation area. Similar things can be said for wollastonite and Ca₂SiO₄ saturation areas.

Isothermal diagrams

Figures 12 and 13 show the effect of various contents of Al₂O₃ on the liquid regions of FeO-Fe₂O₃-CaO-SiO₂ system at 1300°C and 1250°C respectively and at oxygen partial pressure of 10⁻⁸ atm. The liquid region of the same system without Al₂O₃ is also shown. As can be seen, alumina stabilizes the spinel (magnetite) phase and significantly decreases the liquid region at magnetite precipitation area and consequently increases the risk of magnetite precipitation. This explains the problem of magnetite (spinel) precipitation encountered in industrial practices of intermediate oxygen potentials such as copper continuous converting for slags of high Al₂O₃ content. As seen in the figures, however, alumina increases the liquid region in all other saturation areas (Ca₂SiO₄, wollastonite, silica and Ca₂Fe₂O₅). It suppresses the formation of solid silica by moving the silica boundary toward lower silica content, but, as mentioned above, this is associated with an increase of the liquidus temperature in the spinel surface and not with a decrease. It is also noteworthy in Figure 12 the transition from the wustite precipitation area to the spinel one along with the increase of alumina contents.

Oxidative and reductive conditions

There is also a fundamental difference between the effect of Al₂O₃ in oxidative smelting and converting conditions and reductive conditions. This is shown in Figure 14 which clearly demonstrates that, at a constant Fe/SiO₂ ratio, Al₂O₃ decreases the liquidus temperature in reductive conditions (olivine precipitation surface) but it increases it in oxidative conditions (spinel saturation surface).

EFFECT OF MgO ON THE LIQUIDUS SURFACE OF FeO-Fe₂O₃-SiO₂-CaO SLAG

Experimental Verification of Model Predictions

The data of Ducret (21) seem to be the only measurements of the liquidus temperatures of CaO-MgO-FeO-Fe₂O₃-SiO₂ system at controlled intermediate oxygen potentials (CO₂/CO=7.4: around 10⁻⁸atm) for some combinations of CaO and MgO varying respectively 3-9 and 3-12% at approximately Fe/SiO₂ ratio of 1.46. The author uses nickel crucible for quenching experiments but does not measure the complete chemical composition

of each individual sample after equilibrating and quenching. He measures only three samples for Fe^{2+} and total Fe after quenching and, by assuming (without any measurements) 4% NiO in the slag, he calculates the rest of the sample as SiO_2 . Based on this assumption he reports that an average decrease of Fe/ SiO_2 ratio of about 8.2% normally occurs. This decrease is then applied to all other samples. The Fe/ SiO_2 ratio determined according to this procedure is only approximate. Furthermore the use of the original composition of MgO and CaO without any recalculation toward the slag after quenching (loss of iron in nickel crucible) also makes approximate their content in the slag. For these reasons, taking also into account, the elemental error of $\pm 2\%$ of the energy dispersive system (EDS) used for the chemical composition as well as other normal experimental errors, it can be said that the overall results at these oxygen partial pressures seem not to be accurate. However, Ducret data are useful since, at this oxygen potential, at 0 and 3 % MgO and within the interval of 2-10% CaO, they agree qualitatively with the model predictions. The author reports that at these oxygen potentials both MgO and CaO increase the slag liquidus temperature. This is in agreement with the model predictions in the spinel saturation area. In fact, Ducret considers this area as wustite, but he admits that due to large errors in EDS oxygen analysis this phase can be any other form of iron compound such as magnetite, which is in fact in agreement with the present model.

There are practically no other experimental liquidus data on CaO-FeO- Fe_2O_3 - SiO_2 -MgO system at intermediate oxygen potentials and especially in the spinel surface, besides the liquidus data of by Bowen & Shairer (22) and Muan & Osborn (23) on its MgO-FeOx- SiO_2 sub-system at various CO_2/H_2 , which agree with the model.

It is estimated that the present model is the best possible evaluation of the liquidus temperatures at the present conditions of lack of the experimental liquidus data as well as some existing disagreements in the solid phases. More experimental work is however suggested to verify the model predictions or possibly calibrate it if found necessary.

Polythermal Projection Diagrams

Figures 15 and 16 present two examples of the liquidus surface of CaO-FeO- Fe_2O_3 - SiO_2 -MgO containing 1 and 3% MgO at oxygen potential of 10^{-8} atm. It can be seen that seven primary crystalline saturation areas are present i.e. spinel, alpha- Ca_2SiO_4 , wollastonite, $\text{Ca}_3\text{Si}_2\text{O}_7$, silica, olivine and wustite, and each of them has their own characteristics. The following important points are worthy of note.

At a constant Fe/ SiO_2 ratio, MgO increases the slag liquidus temperature at intermediate oxygen potentials in the spinel saturation area. This increase is non-uniform and varies from 7 to 9 degrees per 1% MgO. It can also be seen that additions of MgO enlarge the spinel saturation area and suppresses the formation of solid silica by moving the silica boundary toward lower silica content. This is associated, however, with an increase of the liquidus temperature in the spinel surface and not with a decrease. Only, if the original composition of the slag lies in the silica surface, which, as mentioned above, is a rare case in industrial practice, additions of MgO decrease the liquidus temperature and suppress the silica saturation area. Similar things can be said for wollastonite and Ca_2SiO_4 saturation areas. However, opposite effects are visible on the olivine and wustite phases. Olivine becomes stable only at around MgO=3%. MgO stabilize both olivine and wustite and enlarge their saturation areas.

Isothermal diagrams

Figure 17 shows the effect of various contents of MgO on the liquid regions FeO-Fe₂O₃-CaO-SiO₂ system at 1250°C and oxygen partial pressure of 10⁻⁸ atm. The liquid region of the same system without MgO is also shown. As can be seen, MgO stabilizes the spinel (magnetite) phase, decreases significantly the liquid region at spinel precipitation area and consequently increases the risk of spinel (magnetite) precipitation. This explains the problems encountered in industrial practices with magnetite (spinel) precipitation for slags of high MgO content. However, as seen in the figure, MgO suppresses the formation of solid silica by moving the silica boundary toward lower silica content but, as mentioned above, this is associated with an increase of the liquidus temperature in the spinel surface and not with a decrease.

Oxidative and reductive conditions

There exists a difference between the effect of MgO in oxidative smelting and converting conditions and reductive conditions. This is shown in Figure 18 which clearly demonstrates that, at a constant Fe/SiO₂ ratio, MgO increases the liquidus temperature in both reductive (olivine surface) and in oxidative conditions (spinel surface) but this effect is much more pronounced in reductive conditions.

EFFECT OF Cu₂O ON THE LIQUIDUS SURFACE OF FeO-Fe₂O₃-SiO₂-CaO SYSTEM

Experimental Verification of Model Predictions

There are practically no experimental data on the liquidus temperature of the FeO-Fe₂O₃-SiO₂-CaO-Cu₂O slag especially in the spinel saturation area. Consequently the present model is based on several activity data in the copper containing spinel phase as well as the copper solubility data in the slag in equilibrium with pure liquid copper or Cu-Au alloys and/or saturated with SiO₂, which are all reproduced by the model.

Although it is estimated that this model is the best possible evaluation of the liquidus temperatures at present conditions of a lack of the experimental data, more experimental work is necessary to verify the model predictions or possibly to calibrate it if found necessary. For example some measurements of the liquidus temperature in the spinel saturation area at low oxygen potentials are necessary to fill the gap of the previous works.

Polythermal Projection Diagrams

Figures 19 and 20 show two examples of the liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-Cu₂O system at oxygen potential of 10⁻⁶ atm. The first one corresponds to a content of 2% Cu₂O in the slag and the second one to copper saturation conditions. It can be seen that five primary crystalline saturation areas are present i.e. spinel, alpha-Ca₂SiO₄, wollastonite, Ca₃Si₂O₇ and silica and each of them has their own characteristics. The following important points are worthy of note.

In the spinel saturation area, at constant Fe/SiO₂ ratio, Cu₂O destabilizes the spinel phase and decreases the liquidus temperature of the slag by approximately 3 to 5 degrees per 1% Cu₂O. This effect, which is not necessarily a uniform one, helps to reduce the risk of spinel (magnetite) precipitation during smelting and converting. Cu₂O suppresses slightly the silica saturation area and also slightly stabilizes Ca₂SiO₄ and wollastonite saturation areas.

Similar effects are visible in the diagram of CaO-FeO-Fe₂O₃-SiO₂-Cu₂O system in equilibrium with liquid copper except that spinel saturation area is only slightly more stabilized. It should also be noted in Figure 20 that the content of Cu₂O in the slag at the saturation of a second phase varies approximately from 8 to 10 wt% Cu₂O.

Isothermal diagrams

Figure 21 shows the effect of various contents of Cu₂O on the liquid regions FeO-Fe₂O₃-CaO-SiO₂ system at 1300°C at oxygen partial pressure of 10⁻⁶ atm. The liquid region of the same system without Cu₂O is also shown. As can be seen, Cu₂O increases the liquid region in the spinel precipitation area and consequently decreases the risk of spinel (magnetite) precipitation. Cu₂O also suppresses the formation of solid silica by moving the silica boundary toward lower silica content and, in this case, this is associated with a decrease of the liquidus temperature in the spinel surface.

DISCUSSION

As mentioned above, confusion exists in the recent literature and in industrial practice concerning the effect of minor oxides such as CaO, MgO and Al₂O₃ on the liquidus temperature of the CaO-FeO-Fe₂O₃-SiO₂ slag. Several global assertions have recently been made on the effect of these components but they ignore the influence of oxygen potentials pertaining to particular processes, the particularities of certain laboratory procedures or the positioning of the initial slag composition. For instance, in a last year publication related to copper continuous converting(24) (PO₂ 10⁻⁸-10⁻⁶ atm) it is stated that “the presence of small amounts of CaO, MgO and Al₂O₃ would lower the melting point of fayalite slags”. This incorrect conclusion comes as a result of an apparent misinterpretation of the data of Kim and Sohn (25) and Altman (26) who have measured the ferric/ferrous ratio of silica saturated iron silicate slags at constant temperature but at the resulting various silica contents. This procedure ignores the effect of silica and makes the results directly incomparable at constant Fe/SiO₂ ratios. Instead, as can be gauged from the diagrams presented in this work at intermediate oxygen potentials, at a constant Fe/SiO₂ ratio, CaO, MgO and Al₂O₃ increase the liquidus temperature of silica non-saturated “iron silicate” slags in the spinel surface and increase the risk of spinel (magnetite) precipitation. The origin of the confusion in the literature comes from the fact that the experiments have always been carried out at silica saturation. At these conditions the addition of CaO, would decrease the liquidus temperature of the slag only in the direction of silica saturation curve along with simultaneous and continuous decrease of Fe/SiO₂ ratio, which adjust itself during the experiments. This is clearly shown in Figures 4 and 5, where the liquidus temperature is decreased only along the silica saturation curves. The same thing can be said for the effect of MgO and Al₂O₃. As shown above, both increase the liquidus temperature in the spinel (magnetite) surface, decrease the liquid region of the homogeneous slag especially in the spinel surface and

increase the risk of spinel precipitation. From the figures presented in this work and especially Figures 12-14 and 17-18 it can be stated that the solution of CaO, MgO and Al₂O₃ suppresses the formation of solid silica and moves the silica boundary toward lower silica content. However this is associated with an increase of the liquidus temperature in the spinel surface and not with a decrease. Only when the original slag composition lies in the silica saturation area, additions of these minor components cause a decrease of the liquidus temperature as long as the composition lies in this area. Nevertheless, almost none of the slags in industrial processes at intermediate oxygen potentials have the original composition in the silica saturation area since, as explained above, the normal minor oxides that come from the feed materials suppress this area and place the original composition in the spinel surface. From this point on the additions of CaO, MgO and Al₂O₃ would only increase the liquidus temperature of the slag at constant Fe/SiO₂ ratio. These effects can be gauged directly from the above-presented set of diagrams, which due to their simplicity and comprehensibility not only describe quantitatively and selectively the effect of minor components and oxygen potentials on the liquidus temperature of multicomponent slags but also easily defuse the confusion found in literature.

CONCLUSIONS

The liquidus surface of CaO-FeO-Fe₂O₃-SiO₂ slag containing Al₂O₃, MgO and Cu₂O was quantified at various intermediate oxygen potentials by the means of a thermodynamic model and a special new type of multicomponent phase diagrams. The effect of oxygen potentials and minor oxides were also quantified and the confusion that exists in today's literature concerning this effect was clarified. It was shown that important differences exist between the liquidus surfaces of this system in reductive and oxidative conditions and the effect of minor components can be fundamentally different in reductive and oxidative conditions. The results of this work are already used to determine the availability of newly proposed "ferrous calcium silicate slags" (4,5). With further proper extensions, these results can also be useful, not only for other non-ferrous processes but also for the understanding of several ferrous metallurgical processes such as iron ore sintering and sinter reduction in the blast furnace (5). These subjects as well as the quantification of the effect of other minor oxides are ongoing research (27) and may be published in the future.

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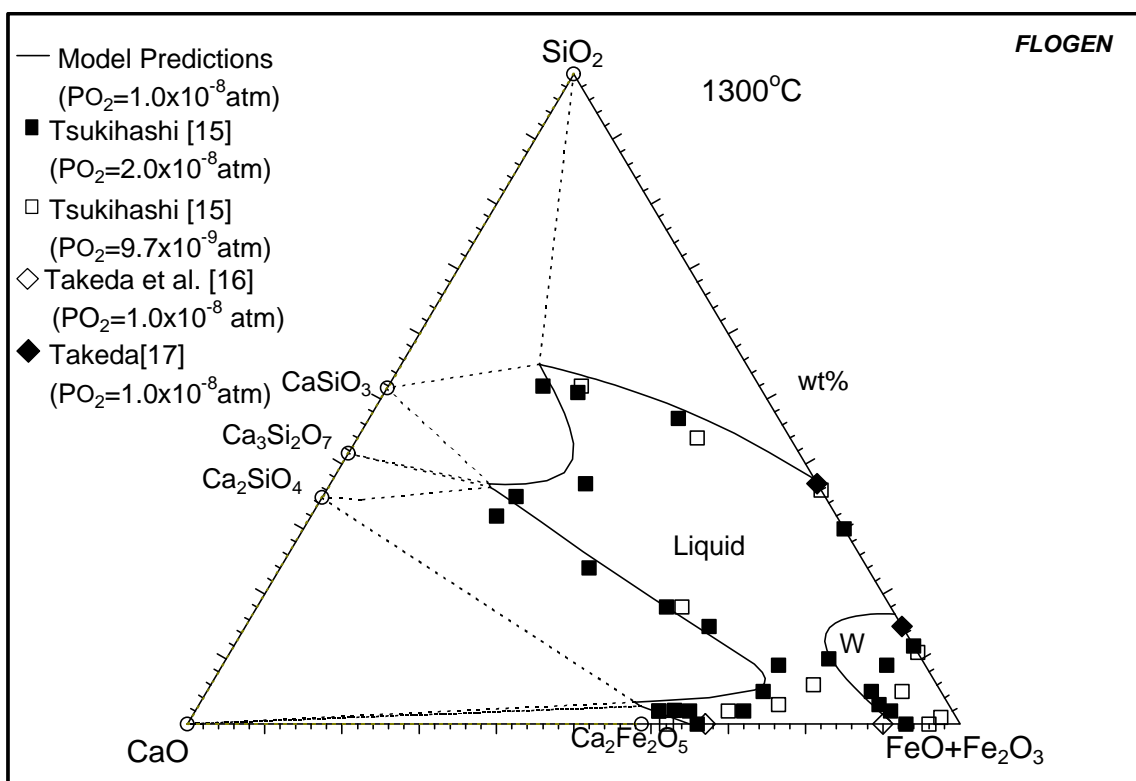


Figure 1 - Liquid region of CaO-FeO-Fe₂O₃-SiO₂ slag at 1300°C and PO₂ of 10⁻⁸ atm according to model predictions and available experimental data

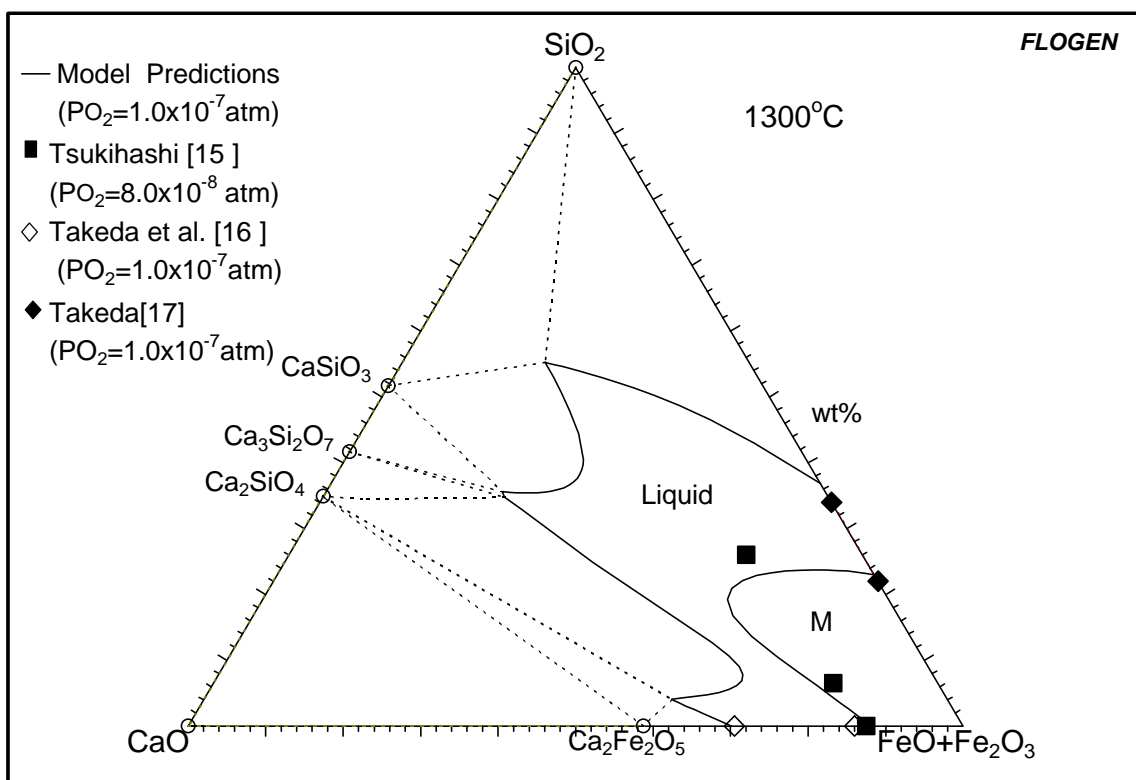


Figure 2 - Liquid region of CaO-FeO-Fe₂O₃-SiO₂ slag at 1300°C and PO₂ of 10⁻⁷ atm according to model predictions and available experimental data

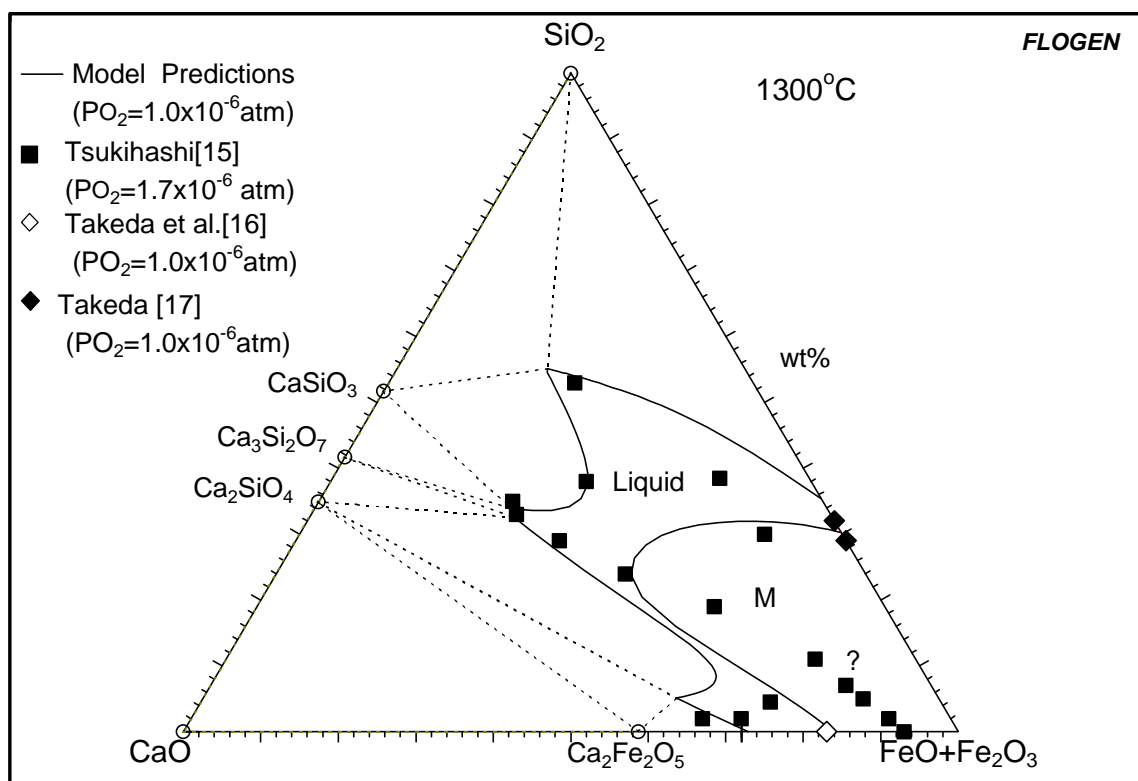


Figure 3 - Liquid region of CaO-FeO-Fe₂O₃-SiO₂ slag at 1300°C and PO_2 of 10^{-6} atm according to model predictions and available experimental data

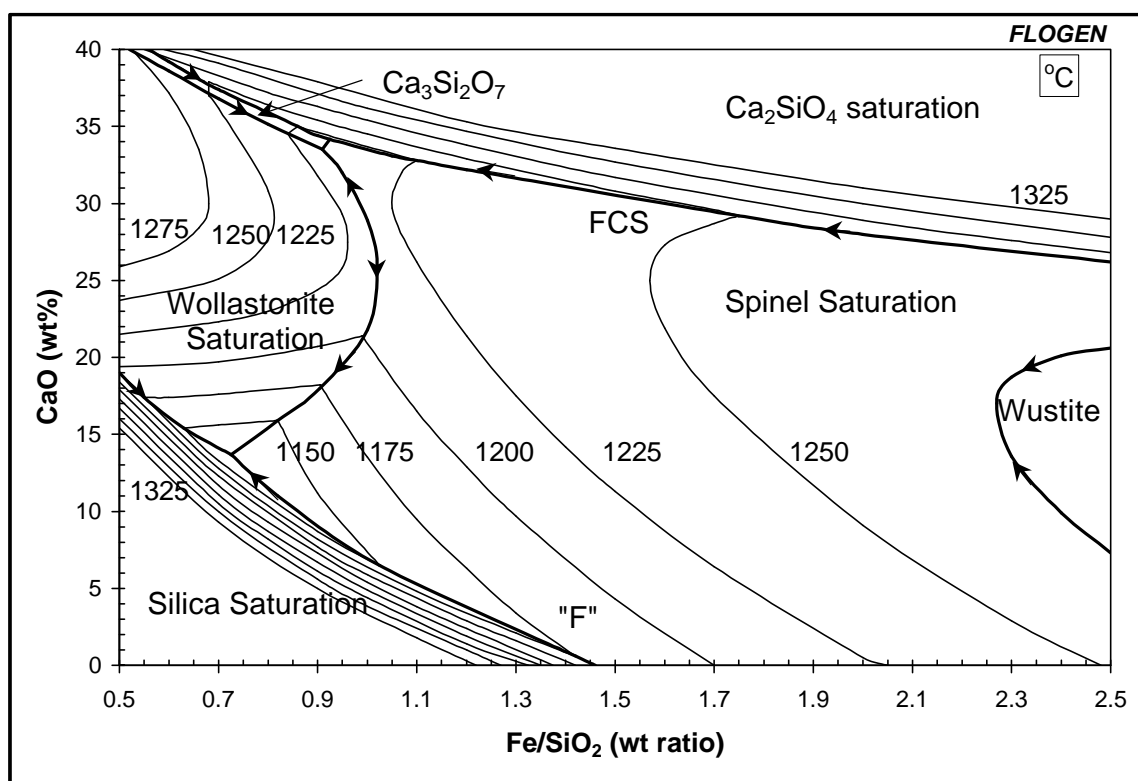


Figure 4 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂ slag at PO_2 of 10^{-8} atm

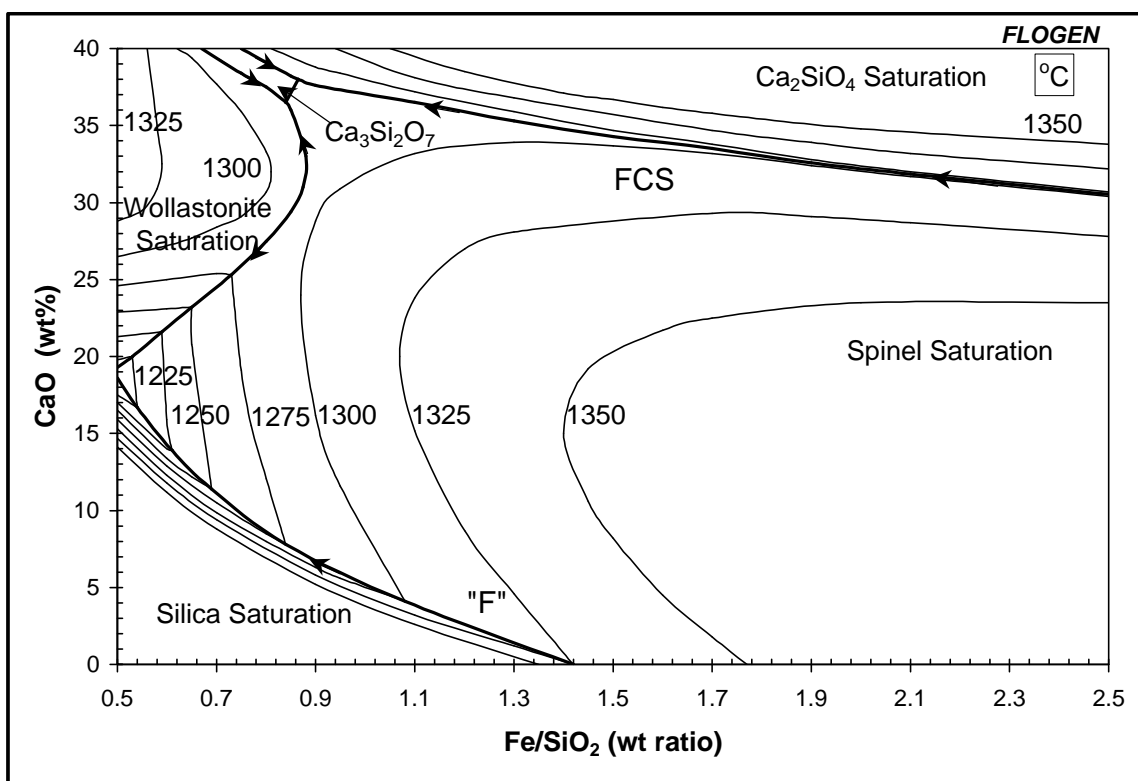


Figure 5 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂ slag at PO₂ of 10⁻⁵ atm

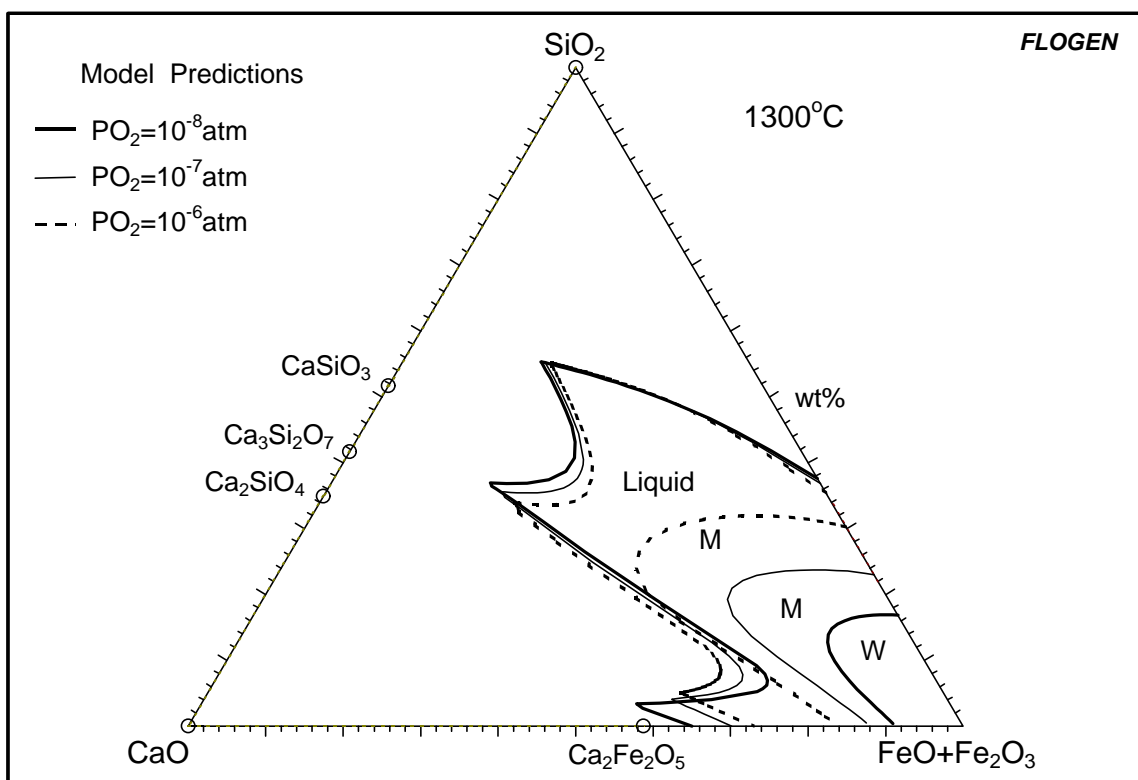


Figure 6 – Effect of oxygen potential on the liquid regions of CaO-FeO-Fe₂O₃-SiO₂ slag at 1300°C.

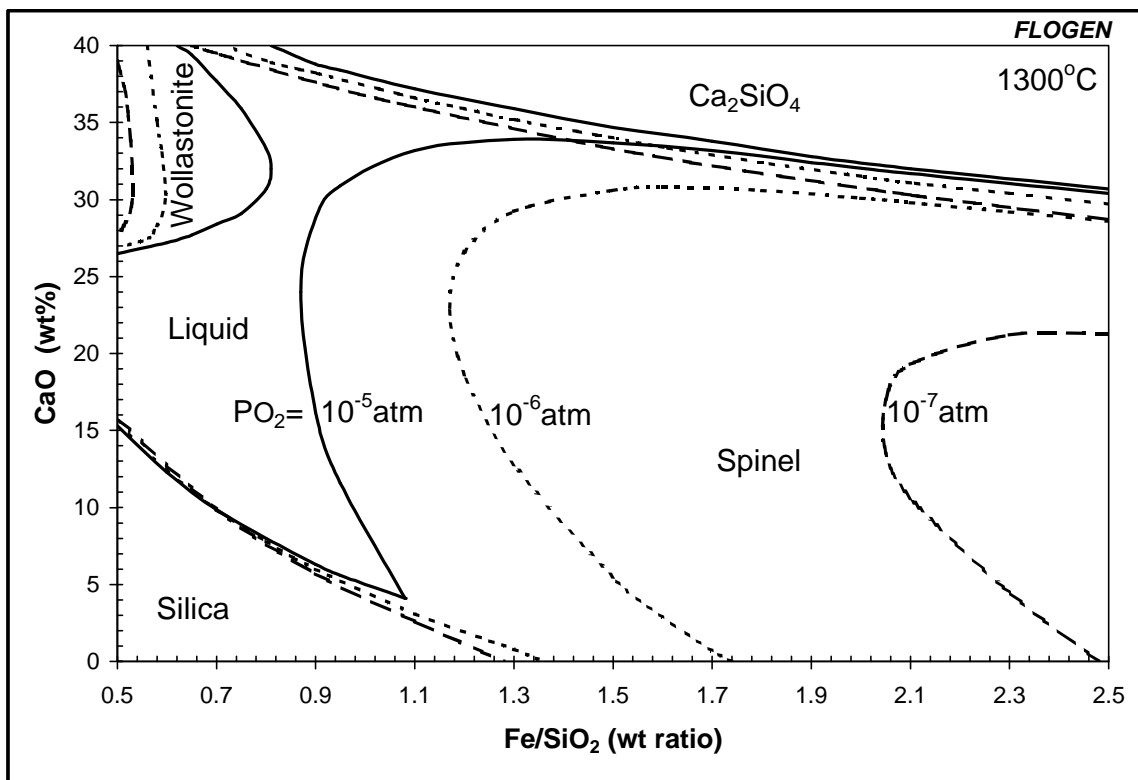


Figure 7 - Liquid regions of CaO-FeO-Fe₂O₃-SiO₂ slag at 1300°C and various oxygen potentials

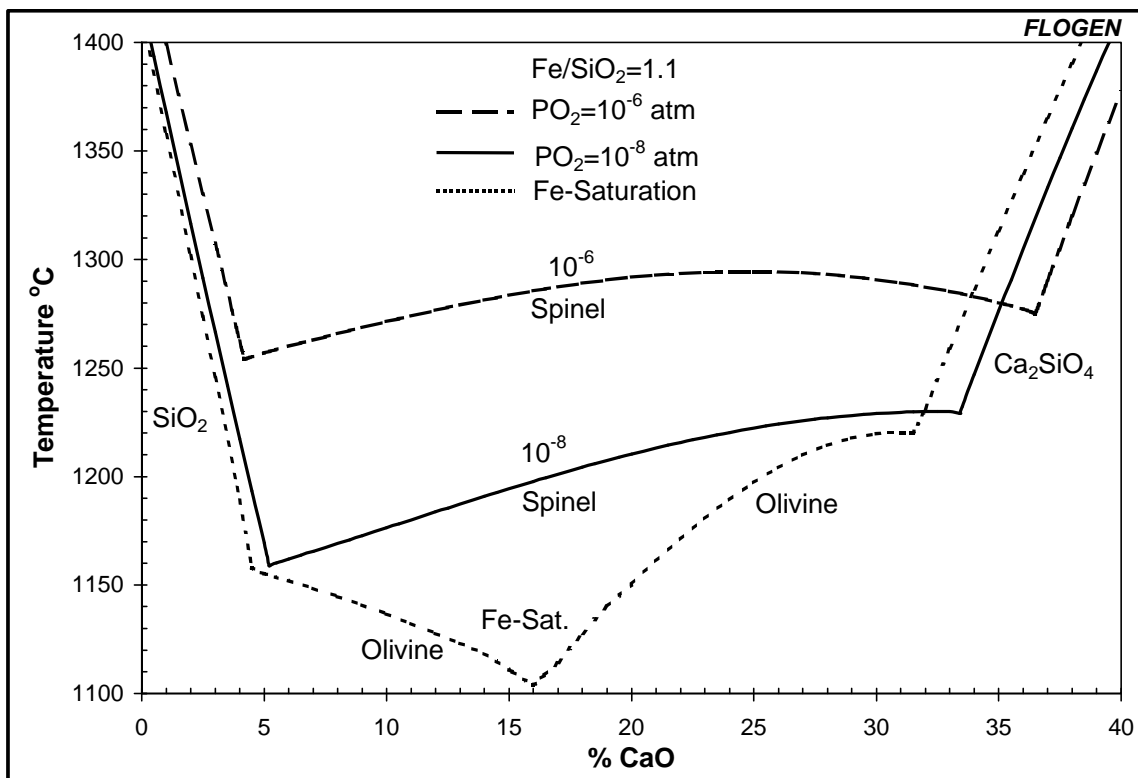


Figure 8 – Effect of CaO on the liquidus temperature of CaO-FeO-Fe₂O₃-SiO₂ slag at various oxygen potentials

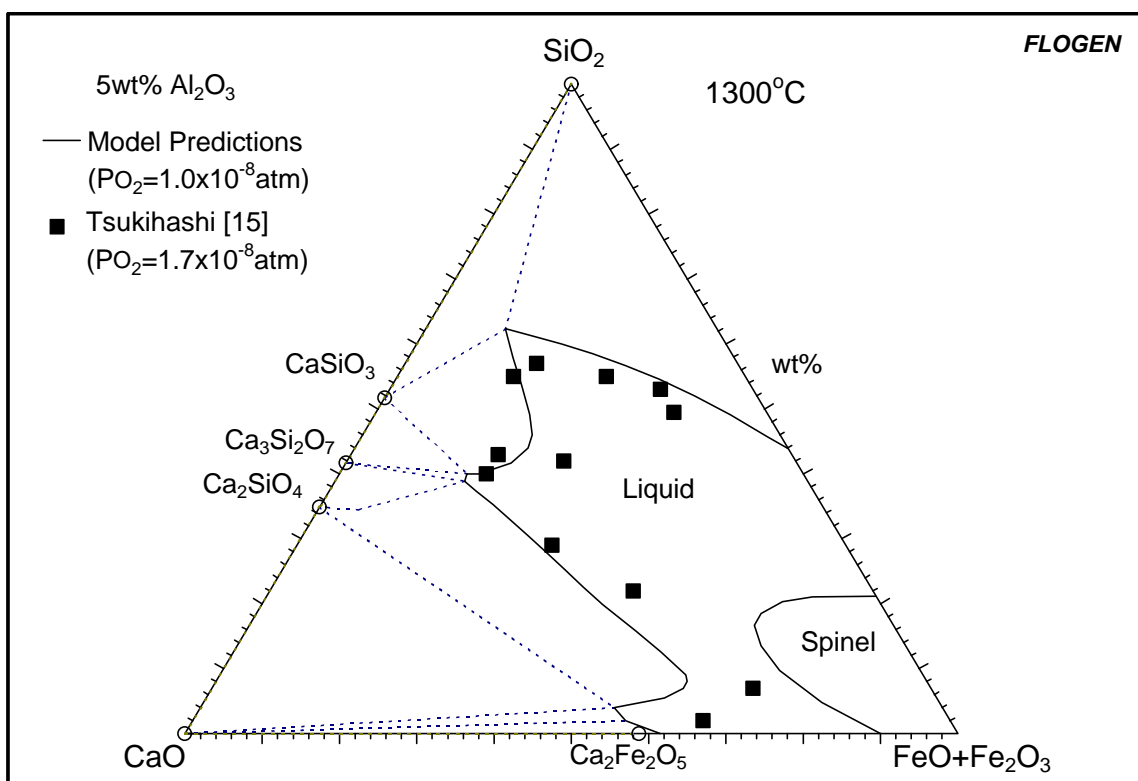


Figure 9 - Liquid region of $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ slag at 5wt% Al_2O_3 , 1300°C and PO_2 of 10^{-8} atm according to model predictions and experimental data

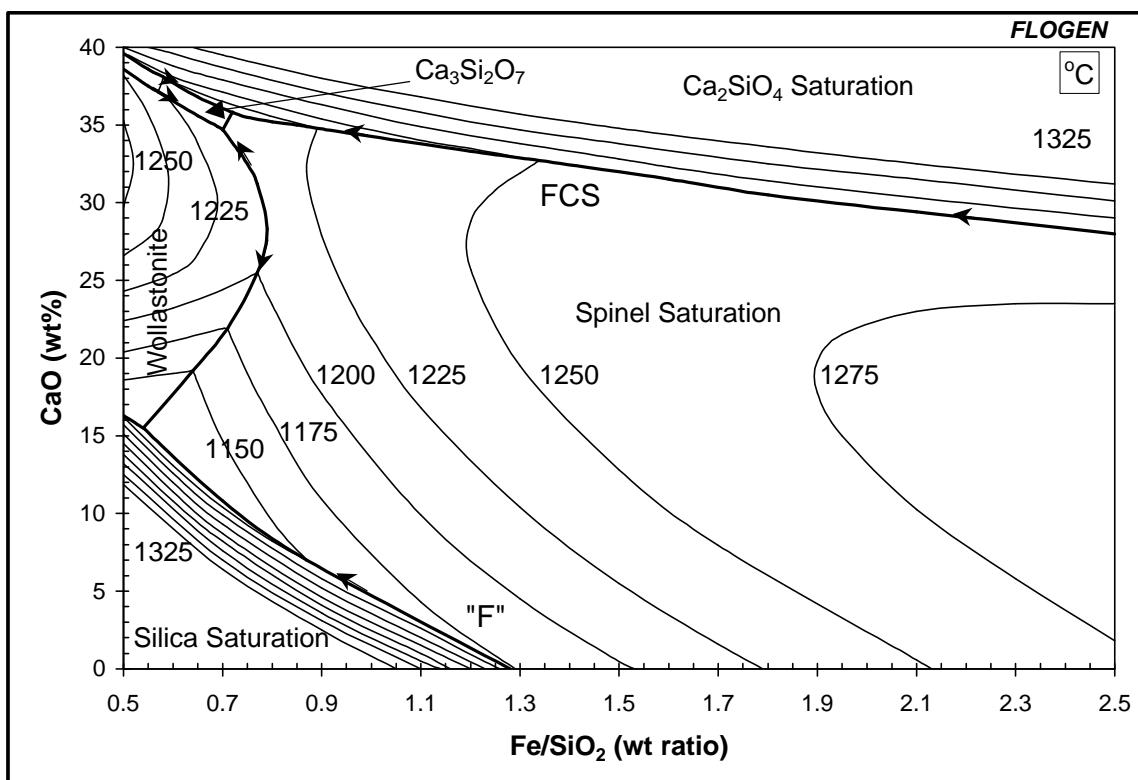


Figure 10 - Liquidus surface of $\text{CaO-FeO-Fe}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ slag at PO_2 of 10^{-8} atm and 3 wt% Al_2O_3

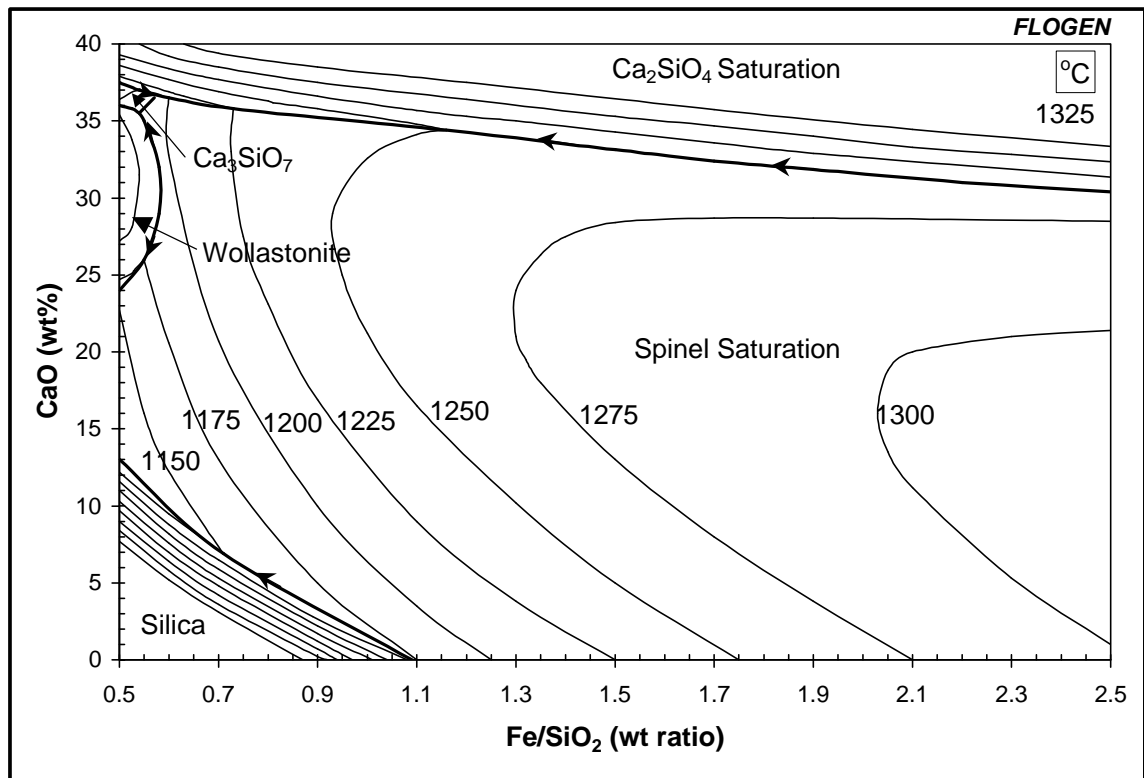


Figure 11 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃ slag at PO₂ of 10⁻⁸atm and 7 wt% Al₂O₃

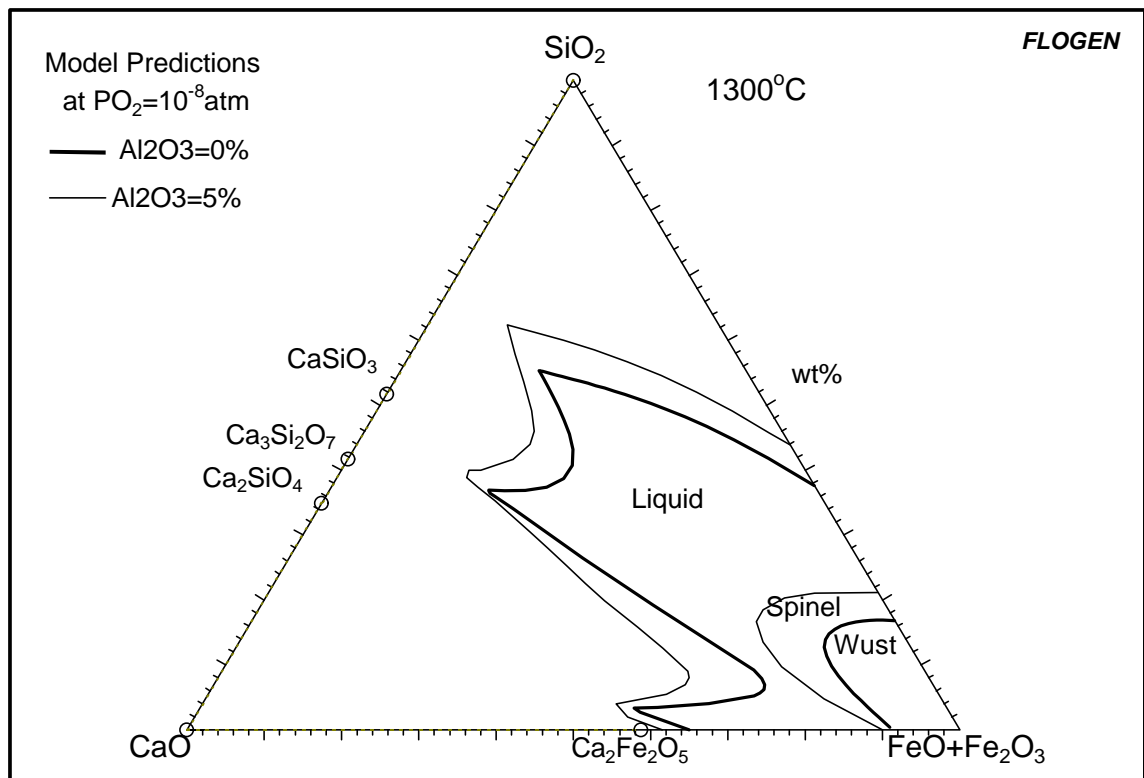


Figure 12 – Effect of Al₂O₃ on the liquid regions of CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃ slag at 0 and 5% Al₂O₃, at 1300°C and PO₂ = 10⁻⁸ atm.

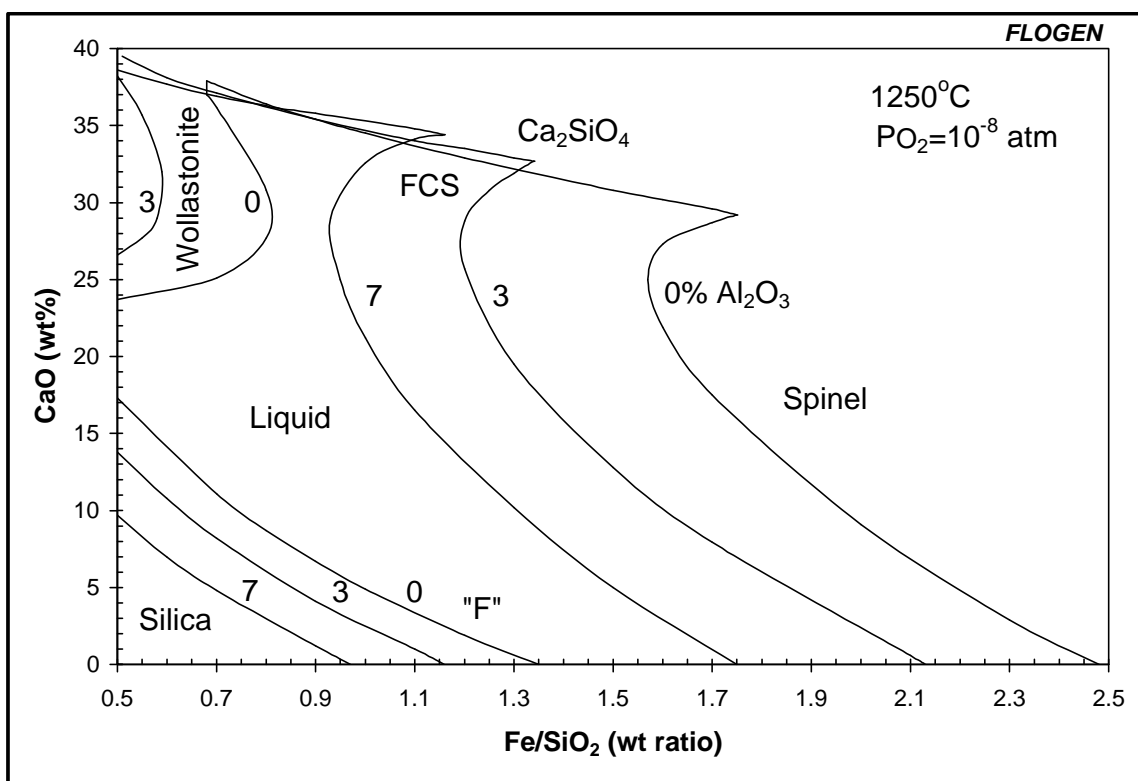


Figure 13 - Liquid regions of CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃ slag at 0, 3 and 7wt% Al₂O₃, 1250°C and PO₂ of 10⁻⁸atm

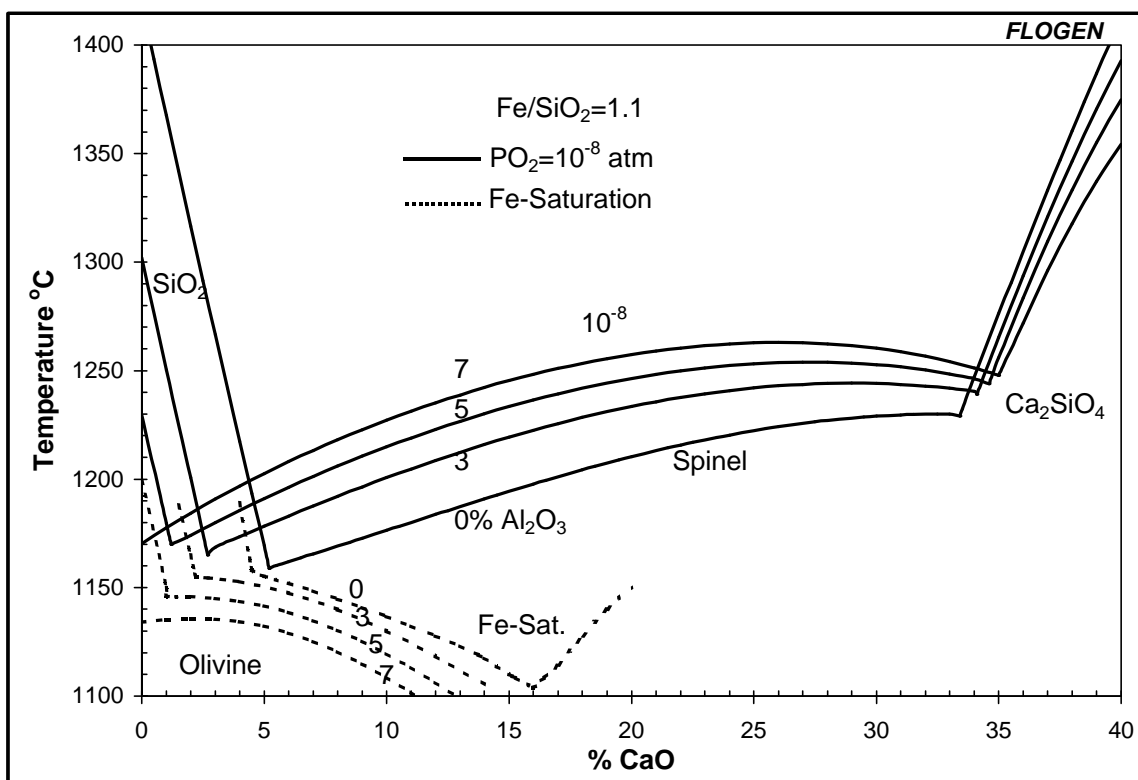


Figure 14 – Effect of Al₂O₃ on the liquidus temperature of CaO-FeO-Fe₂O₃-SiO₂-Al₂O₃ slag at Fe/SiO₂=1.1 and various oxygen potentials

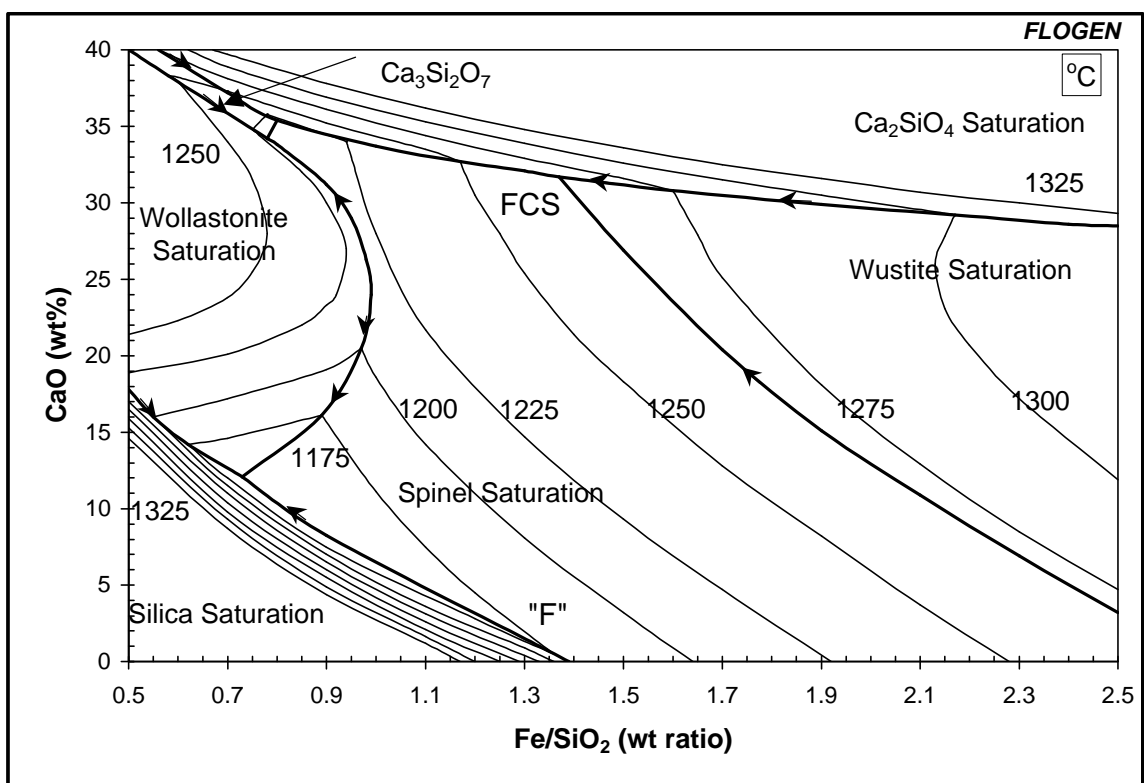


Figure 15 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-MgO slag at PO₂ of 10⁻⁸ atm and 1wt% MgO

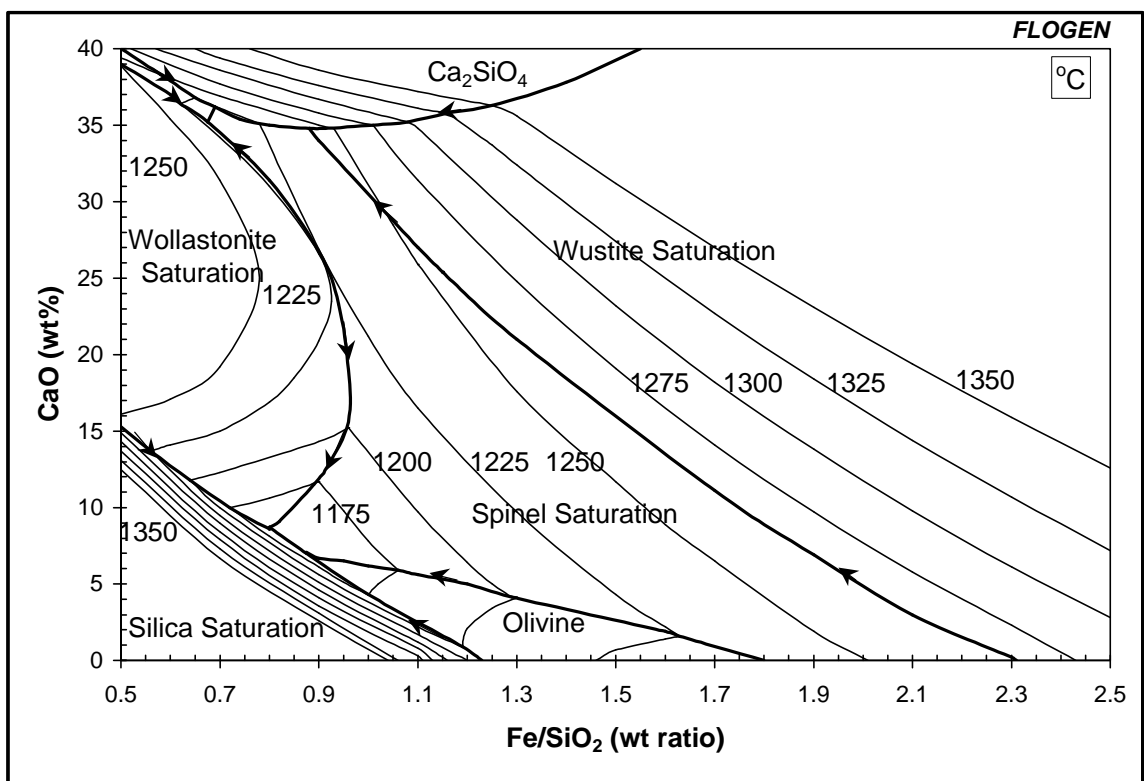


Figure 16 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-MgO slag at PO₂ of 10⁻⁸ atm and 3wt% MgO

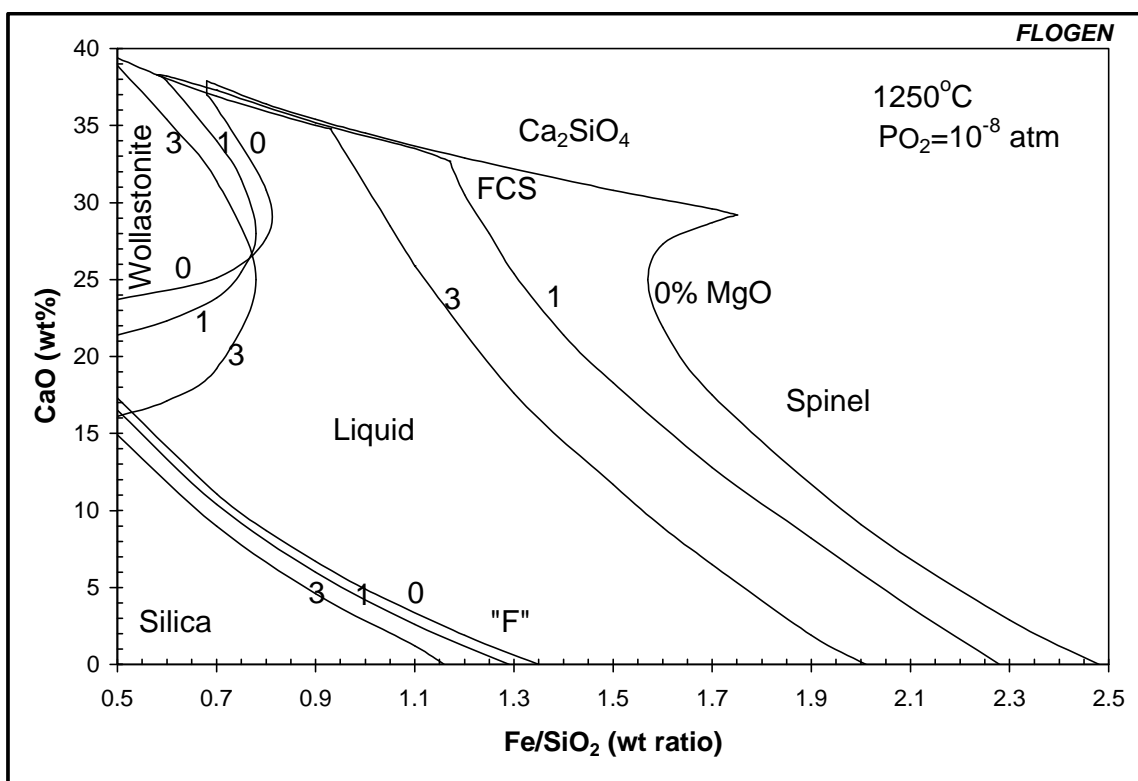


Figure 17 – Effect of MgO on the liquid region of CaO-FeO-Fe₂O₃-SiO₂-MgO slag at PO_2 of 10^{-8} atm and 1250°C

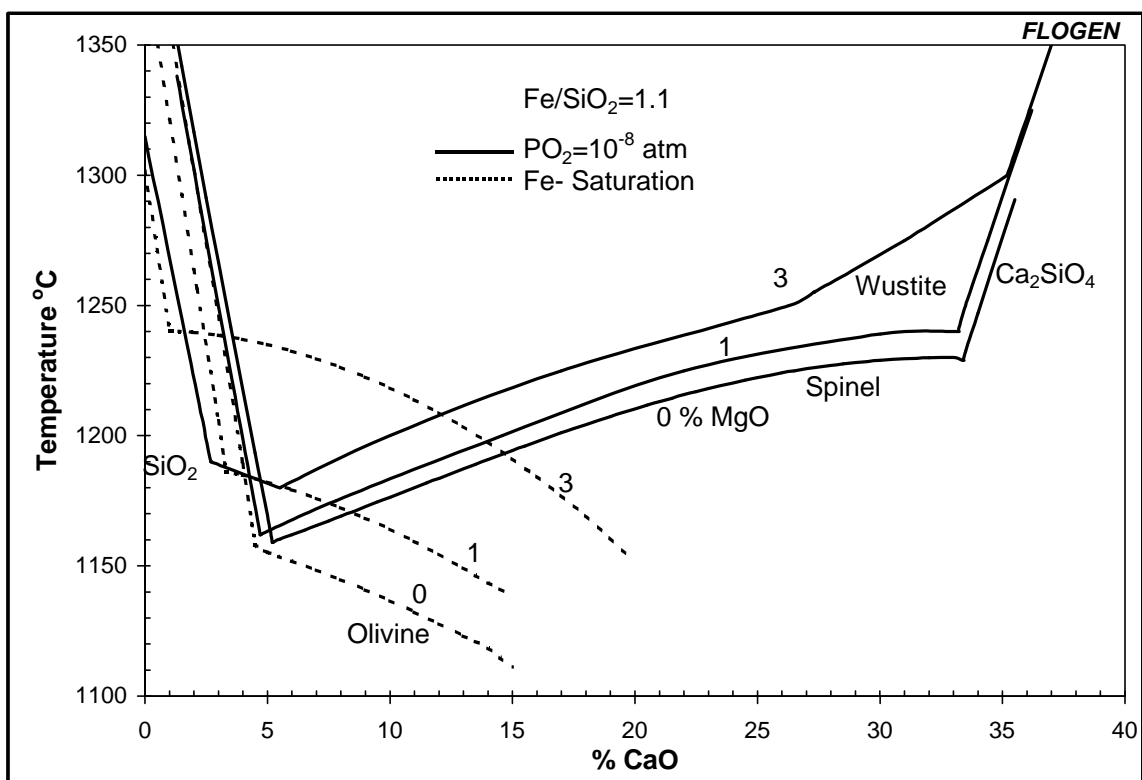


Figure 18 - Effect of MgO on the liquidus temperature of CaO-FeO-Fe₂O₃-SiO₂-MgO slag at Fe/SiO₂=1.1 and various oxygen potentials

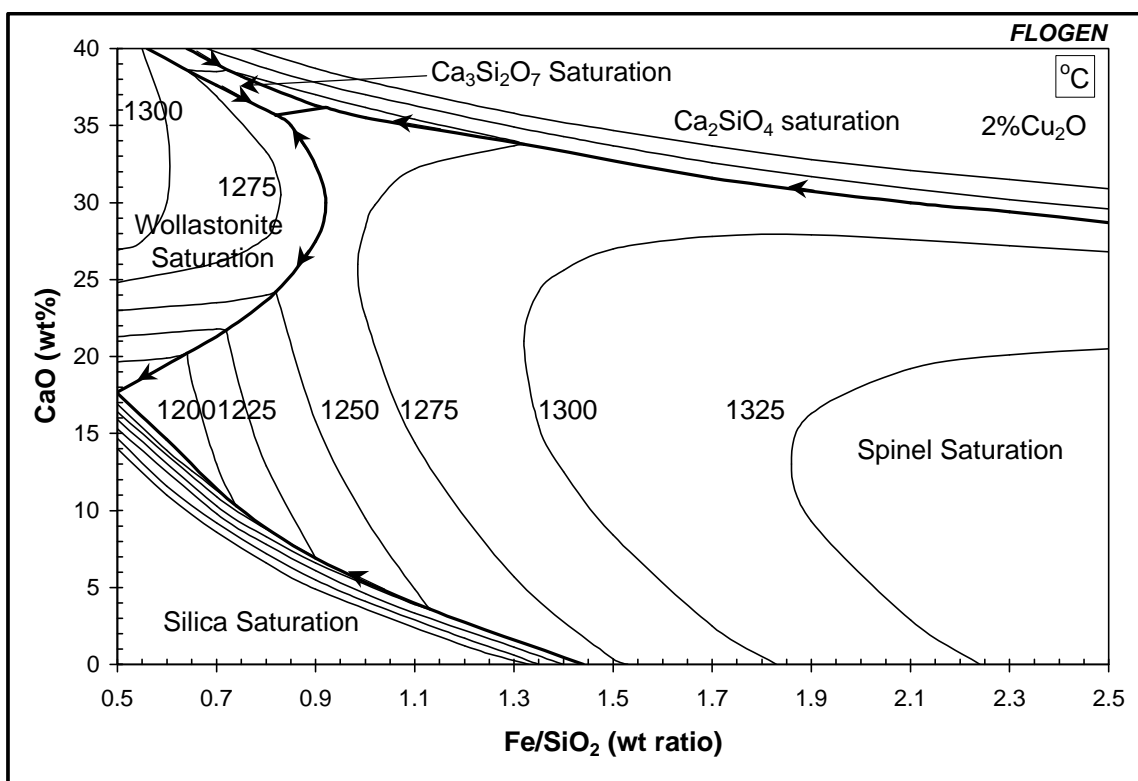


Figure 19 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-Cu₂O slag at PO₂ of 10⁻⁶ atm and 2wt% Cu₂O

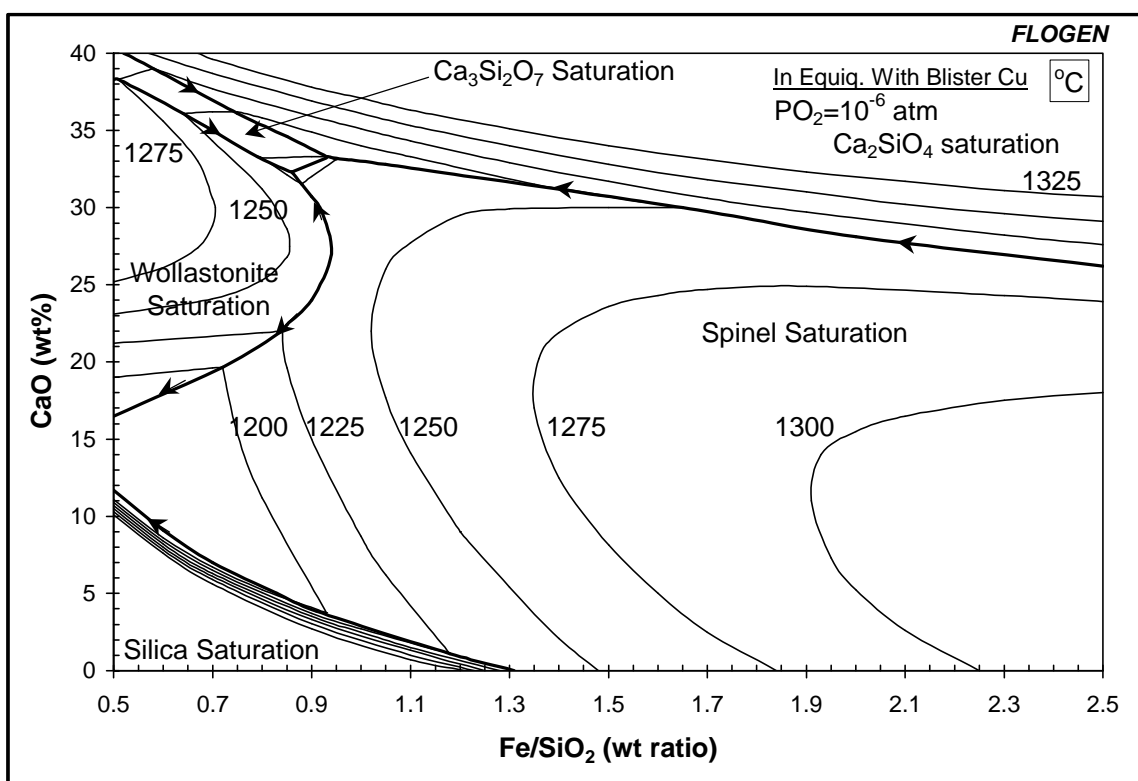


Figure 20 - Liquidus surface of CaO-FeO-Fe₂O₃-SiO₂-Cu₂O slag in equilibrium with blister copper at PO₂ of 10⁻⁶ atm.

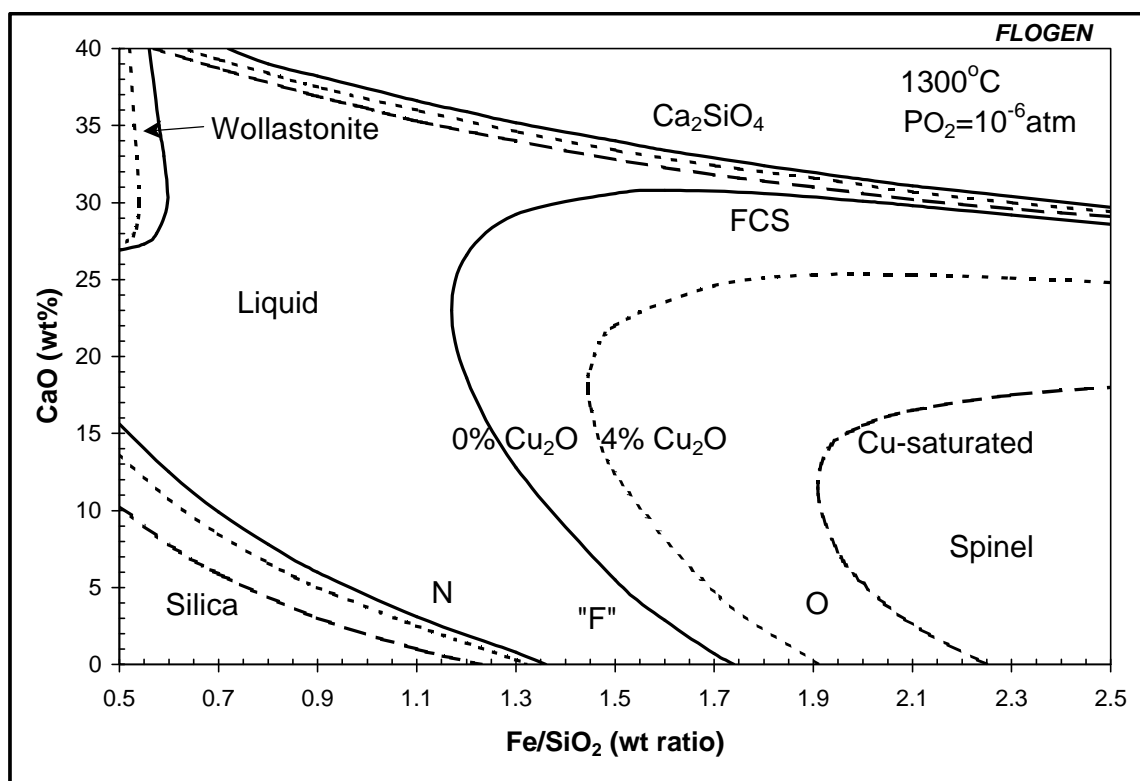


Figure 21 – Effect of Cu₂O on the liquid regions of CaO-FeO-Fe₂O₃-SiO₂-Cu₂O Slag at 1300°C and PO₂ of 10⁻⁶ atm (N: Noranda; O-Olympic Dam)